

Supporting information

Probing structural consequences of N9-alkylation in silver-adenine frameworks

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General Procedures: ^1H and ^{13}C NMR spectra were obtained on a JEOL-DELTA2 500 model spectrometer operating at 500MHz. The spectra were recorded in DMSO- d_6 solution and the chemical shifts were referenced with respect to tetramethylsilane. High resolution (ESI $^+$ mode) mass spectra were obtained on Waters, Q-Tof Premier Micromass HAB 213 mass spectrometer, Department of Chemistry, IIT Kanpur, India. Solvents were evaporated using rotary evaporator under reduce pressure. n-Propyl bromide, n-hexyl bromide, n-nonyl bromide and n-benzyl bromide was purchased from Spectrochem Pvt. Ltd. Mumbai and used without further purification. All solvents were distilled prior to use using standards procedures.

Synthesis of 9-propyladenine: Experimental details for the synthesis of 9-PA have been reported earlier.¹ A similar protocol was followed and the purity of product so obtained was confirmed by spectroscopic analysis.

Synthesis of 9-hexyladenine: Adenine (1.0g, 1eq) was suspended in DMF (45mL) followed by addition of NaH (60% paraffin, 355mg, 1.2eq) and stirring under N2 atmosphere for 30 min, after this n-hexyl bromide ($d=1.174$ g/ml, 2.08 ml, 1eq) is added and stirred for 15 hours under N2 atmosphere. After this time DMF was evaporated at 60°C under high vacuum and compound was purified by column chromatography eluting with methanol/DCM to afford white powder

(1.35g, 83.19% Yield). HRMS: ($M+1$)⁺ calculated: 220.1562, Found: 220.1564; M.P.209-210°C; ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ(ppm) 0.77-0.78 (t, 3H, CH₃), 1.18-1.19 (m, 6H, (CH₂)₃) 1.72-1.75 (m, 2H, CH₂), 4.06-4.09 (t, 2H, NCH₂), , 7.16 (s, 2H, NH₂), 8.09 (s, 1H, C8-H), 8.10 (s, 1H, C2-H); ¹³C NMR (125 MHz, DMSO-*d*₆, 25°C): δ (ppm) 14.35, 22.47, 26.15, 29.83, 31.16, 43.39, 119.21, 141.38, 150.02, 152.84, 156.42.

Synthesis of 9-nonyladenine: Adenine (1.0g, 1eq) was suspended in DMF (45mL) followed by addition of NaH (60% paraffin, 355mg, 1.2eq) and stirring under N₂ atmosphere for 30 min, after this n-nonyl bromide (d=1.086 g/ml, 1.41ml, 1eq) is added and stirred for 15 hours under N₂ atmosphere. After this time DMF was evaporated at 60°C under high vacuum and compound was purified by column chromatography eluting with methanol/DCM to afford white powder (1.2 g, 62% Yield). HRMS: ($M+1$)⁺ calculated: 262.2032, Found: 262.2032; M.P 122-125°C; ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ (ppm) 0.77-0.80 (t, 3H, CH₃), 1.15-1.29 (m, 12H, (CH₂)₆), 1.72-1.75 (m, 2H, CH₂), 4.06-4.09 (t, 2H, NCH₂), 7.15 (s, 2H, NH₂) 8.09 (s, 1H, C8-H), 8.09 (s, 1H, C2-H); ¹³C NMR (125 MHz, DMSO-*d*₆, 25°C): δ (ppm) 14.47, 22.60, 26.47, 28.93, 29.09, 29.34, 29.85, 31.74, 43.37, 119.22, 141.36, 150.03, 152.85, 156.44.

Synthesis of 9-benzyladenine: Adenine (1.0g, 1eq) was suspended in DMF (45mL) followed by addition of NaH (60% paraffin, 355mg, 1.2eq) and stirring under N₂ atmosphere for 30 min, after this benzyl bromide (d=1.437 g/ml, 0.836ml, 0.95eq) is added and stirred for 15 hours under N₂ atmosphere. After this time DMF was evaporated at 60°C under high vacuum and compound was purified by column chromatography eluting with methanol/chloroform to afford white powder. HRMS: ($M+1$)⁺ calculated: 226.1093, Found: 226.1096; M.P 230-233; ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ(ppm) 5.33 (s, 2H, CH₂), 7.24–7.30 (m, 5H, 5CH), 7.26 (s, 2H,

NH₂) 8.12 (s, 1H, C8-H), 8.22 (s, 1H, C2-H); ¹³C NMR (125 MHz, DMSO-*d*₆, 25°C): δ (ppm) 46.69, 119.21, 128.04, 128.23, 129.19, 137.68, 141.33, 150.01, 153.19, 156.55.

General procedure for metalation: In a 25 ml round bottom flask, wrapped with aluminum foil, the ligand was dissolved in Methanol and to this added corresponding silver salt solution in water (1 mole equivalent) drop wise with stirring. The white complex started precipitating out with the addition of silver salt solution. Stirring was continued for another one hour. After this time, the precipitate was filtered carefully to avoid direct light, washed with water (4x 5mL) and methanol (4 x 5mL) to remove any traces of unreacted metal salt and ligand. The product so obtained was dried under high vacuum. The yields were almost quantitative.

Synthesis adenine silver complex (1): HRMS: (M+Ag)⁺ calculated: 241.9596, Found: 241.9512; MP > 260°C; ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ (ppm) 5.45 (br, 2H, NH₂), 8.34 (s, 1H, C8-H), 8.54 (s, 1H, C2-H); ¹³C NMR (125 MHz, DMSO-*d*₆, 25°C): δ (ppm) 144.90, 152.30.

Synthesis of 9-propyl adenine silver complex (2): HRMS: (M+Ag)⁺ calculated: 284.0065, Found: 284.0139; MP > 260°C; ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ (ppm) 0.78-0.81 (t, 3H, CH₃), 1.77-1.81 (m, 2H, CH₂), 4.13-4.16 (t, 2H, NCH₂), 7.69 (s, 2H, NH₂) 8.29 (s, 1H, C8-H), 8.36 (s, 1H, C2-H); ¹³C NMR (125 MHz, DMSO-*d*₆, 25°C): δ (ppm) 11.37, 23.25, 45.42, 118.72, 143.28, 149.23, 153.97, 155.75.

Synthesis of 9-hexyl adenine silver complex (3): HRMS: (M+Ag)⁺ calculated: 326.0525, Found: 326.0618, (2M+Ag)⁺ calculated: 545.2019, Found: 545.2126; MP>200°C; ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ (ppm) 0.77-0.79 (t, 3H, CH₃), 1.19-1.25 (m, 6H, (CH₂)₃), 1.74-1.77 (m, 2H, CH₂), 4.13-4.16 (t, 2H, NCH₂), 7.56 (s, 2H, NH₂) 8.23 (s, 1H, C8-H), 8.29 (s, 1H, C2-

H); ^{13}C NMR (125 MHz, DMSO- d_6 , 25°C): δ (ppm) 14.35, 22.45, 26.11, 29.79, 31.13, 43.71, 118.86, 142.74, 149.38, 153.69, 155.93.

Synthesis of 9-nonyl adenine silver complex (4): HRMS: (2M+Ag) $^+$ calculated: 629.2958, Found: 629.2828, (M+Ag) $^+$ calculated: 368.1004, Found: 368.0967; MP>260°C; ^1H NMR (500 MHz, DMSO- d_6 , 25°C): δ (ppm) 0.77-0.80 (t, 3H, CH₃), 1.15-1.19 (m, 12H, (CH₂)₆), 1.74-1.77 (m, 2H, CH₂), 4.13-4.16 (t, 2H, NCH₂), 7.59 (s, 2H, NH₂) 8.24 (s, 1H, C8-H), 8.30 (s, 1H, C2-H); ^{13}C NMR (125 MHz, DMSO- d_6 , 25°C): δ (ppm) 14.47, 22.59, 26.44, 28.92, 29.08, 29.33, 29.83, 31.74, 43.72, 118.85, 142.85, 149.34, 153.72, 155.91.

Synthesis of 9-benzyl adenine silver complex (5): HRMS: (M+Ag+MeCN) $^+$ calculated: 373.0331, Found: 373.0412; MP 158-161°C; ^1H NMR (500 MHz, DMSO- d_6 , 25°C): δ (ppm) 5.41 (s, 2H, CH₂), 7.24–7.30 (m, 5H, 5CH), 7.69 (s, 2H, NH₂) 8.27 (s, 1H, C8-H), 8.45 (s, 1H, C2-H); ^{13}C NMR (125 MHz, DMSO- d_6 , 25°C): δ (ppm) 47.02, 118.74, 128.10, 128.45, 129.28, 137.08, 143.12, 149.17, 154.20, 155.82.

Crystal structure refinement details for 1 and 2: Single Crystal of **1** and **2** were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo KR radiation. The data integration and reduction were processed with the SAINT software.² An absorption correction was applied.³ Structures were solved by the direct method using SHELXS-97 and refined on *F*2 by a full-matrix least-squares technique using the SHELXL-97 program package.⁴ Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters. Crystal structure refinement parameters are given in Table S1 whereas H-bonding parameters are provided in Table S2. CCDC contains the

supplementary crystallographic data for this paper with a deposition number of CCDC **772592**, **772591**, **772587**, **773589**, and **733872** for complex **1**, **2**, **3**, **4**, and **5** respectively. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK. [Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

It should be noted here that nonyl chain in complex **4** is distorted and is solved by using DFIX, SEMU, etc. This disordered leads to problem of ‘Check high and low Ueq’ as compared to the neighbors for C26 and C25 respectively in the check-cif report. Complex **3** also suggest similar alert in the check-cif report for O5, C21’, N2 and C20’ respectively. The terminal alkyl group in both complex **3** and **4** showed abnormally high displacement parameter due to distortion, but all these atoms were refined with anisotropic displacement parameter with a positive definite thermal tensor. This give high Ueq(max)/Ueq(min) ratios for C and H atoms in the check-cif report. Other alert indicates that “coordinates do not form properly connected set” which is common for coordination polymers. In the crystal lattice of **1**, **2** and **3**, water molecules are present and hydrogen atoms are not located on Fourier map due to which ‘A’ level alerts appears, quoting “isolated oxygen atoms”, in the check-cif report.

Table S1: Crystallographic data for complexes **1-5**

Identification	Complex 1	Complex 2	Complex 3	Complex 4	Complex 5
Empirical Formula	C ₅ H ₆ AgN ₇ O ₇	C ₃₂ H ₄₄ Ag ₄ Cl ₄ N ₂₀ O ₁₈	C ₂₂ H ₃₄ Ag ₂ N ₁₂ O ₈	C ₃₀ H ₅₀ Ag ₂ N ₁₂ O ₈	C ₂₆ H ₂₂ AgN ₁₂ O ₃
Mr	384.04	1570.15	810.35	922.56	658.43
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	Orthorhombic
space group	<i>P</i> 2 <i>1/c</i>	<i>F</i> d <i>d</i> 2	<i>P</i> 2 <i>1/c</i>	<i>P</i> 2 <i>1/c</i>	<i>P</i> <i>n</i> <i>m</i> <i>a</i>
a/Å	6.5283(17)	25.146(5)	18.577(5)	20.600(5)	23.072(5)
b/ Å	8.175(2)	25.516(5)	7.346(5)	7.153(5)	19.976(5)

c/ Å	20.896(5)	7.849(5)	25.747(5)	25.954(5)	6.025(5)
α°	90.00	90.000(5)	90.000(5)	90.000(5)	90.000
β°	95.687(4)	90.000(5)	103.013(5)	93.326(5)	90.000
γ°	90.00	90.000(5)	90.000(5)	90.000(5)	90.000
Volume/Å ³	1109.7(5)	5036(4)	3423(3)	3817.9(10)	2777(2)
Z	4	4	4	4	4
D _x /Mg m ⁻³	2.299	2.071	1.572	1.605	1.575
F(000)	752	3104	1632	1888	1332
μ / mm ⁻¹	1.869	1.837	1.202	1.089	0.779
θ range for data collection/°	2.0-28.4	2.27-28.33	2.17-28	1.98-28.32	2.04-25.99
Limiting indices	-8<=h<=8, -10<=k<=9, -22<=l<=27	-30<=h<=33, -33<=k<=33, -10<=l<=8	-23<=h<=24, -9<=k<=9, -34<=l<=20	-27<=h<=24, -8<=k<=9, -34<=l<=33	-22<=h<=28, -22<=k<=24, -7<=l<=7
Reflections collected/unique reflections	6942/2727	7959/2683	20305/7793	23423/9349	14489/2818
R(int)	0.0440	0.0494	0.0974	0.0649	0.0690
Completeness to θ	98.4 %	99.6 %	98.9 %	98.2	99.8
T _{max} / T _{min}	0.7541-0.6132	0.9219-0.8507	0.8892-0.8127	0.8989-0.8117	0.8473-0.7062
Data/restraints/parameters	2727 / 0 / 181	2683 / 16 / 178	8180 / 4 / 413	9349 / 3 / 472	2818 / 0 / 199
Goodness-of-fit on F^2	1.197	1.129	1.004	1.057	1.124
R1 and R2 [$I > 2\sigma(I)$]	0.0440, 0.1151	0.0494, 0.1264	0.0850, 0.2251	0.0649, 0.1339	0.0420, 0.1088
R1 and R2 (all data)	0.0655, 0.1870	0.0702, 0.1964	0.1625, 0.2827	0.1202, 0.1752	0.0588, 0.1281
Largest diff. peak and hole/e.Å ⁻³	1.402-1.843	1.337-1.257	1.319-1.279	1.358-1.006	1.131-0.912
CCDC No.	772592	772591	772587	773589	733872

Table S2: Selected hydrogen bonding distances and bond angle in complexes **1-5**.

C(2)—H(2H)...O(A) [#]	D43A	3H24A	D—B2..A
C(8)—H(8)...O(3)	Complex 1	3.2024	149
N(8)—H(8)...O(4) ^{IV} ⁱ	2.487	3.0566	124
N(8)—H(8A)...O(6)2 ⁱⁱ	2.50	2.8710	148
N(6)—H(6B)...O(5) ⁱⁱⁱ	Complex 2	2.8517	166
N(9)—H(9A)...O(8) ^{IV} ^{iv}	2.48	2.9166(6)	148
N(6)—H(6B)...O(3) ^{vi}	2.58	3.141(19)	124

C(2)—H(2)...O(4) ^{viii}	2.58	3.343(15)	140
C(8)—H(8)...O(1)	2.30	3.19(2)	160
Complex 3			
N(6)—H(1N)...O(2) ^{ix}	1.99(4)	2.856(15)	163(6)
N(6)—H(2N)...O(5)	2.01(6)	2.820(14)	153(5)
N(6A)—H(1NA)...O(w1) ^x	2.57(8)	3.076(13)	119(6)
N(6A)—H(2NA)...O(1) ^x	2.27(8)	3.036(13)	144(8)
C(2)—H(2)...O(1) ^{xii}	2.45	3.200(13)	138
C(2A)—H(2A)...O(5)	2.38	3.169(14)	142
C(2A)—H(2A)...O(6)	2.47	3.347(16)	158
C(8)—H(8)...O(w1) ^x	2.35	3.262(13)	168
C(8)—H(8)...O(6) ^{xii}	2.56	2.966(18)	107
C(8A)—H(8A)...O(w1) ^{xiii}	2.53	3.314(13)	142
C(8A)—H(8A)...O(1) ^{xiii}	2.48	2.972(13)	113
Complex 4			
N(8)—H(2N8)...O(5) ^x	2.15(6)	2.860(8)	143(5)
N(8)—H(1N8)...O(2) ^{xiv}	2.20(7)	2.884(9)	155(7)
N(3)—H(1N3)...O(1)	1.99(10)	2.829(10)	174(9)
N(3)—H(2N3)...O(6) ^{xviii}	2.17(6)	2.896(9)	146(7)
C(1)—H(1)...O(5) ^{xii}	2.47	3.182(10)	134
C(15)—H(15)...O(1)	2.39	3.156(10)	140
C(15)—H(15)...O(3)	2.50	3.406(10)	165
C(19)—H(19)...O(w1) ^{xv}	2.53	3.316(11)	143
C(19)—H(19)...O(6) ^{xvi}	2.45	3.081(10)	125
Complex 5			
N(6)—H(6A)...O(1) ^{xvii}	2.15	2.9893	165
N(6)—H(6A)...O(2) ^{xviii}	2.56	3.2101	133
N(6)—H(6B)...N(7) ^{xix}	2.17	2.9725	156
C(8)—H(8)...O(2) ^{xx}	2.35	3.1688	147
C(10)—H(10A)...O(2) ^{xxi}	2.49	3.3075	142
C(12)—H(12)...N(9)	2.54	2.8762	102

#Symmetry of A (i) 1-x,1/2+y,1/2-z (ii) 1-x,-1/2+y,1/2-z (iii) 1+x,y,z (iv) -1+x,1+y,z (v) x,1+y,z (vi) 1/4+x,1/4-y,5/4+z; (vii) x, y,1+z; (viii) 1/4-x,-1/4+y,3/4+z; (ix) x, 1/2-y,1/2+z; (x) -x,-1/2+y,1/2-z; (xi) -x,1-y,1-z; (xii) -x,-y,1-z; (xiii) x,-1+y,z; (xiv) -x,1/2+y,1/2-z;(xv) x,1/2-y,-1/2+z; (xvi) x,3/2-y,-1/2+z; (xvii) 1/2+x,1/2-y,3/2-z; (xviii) 1/2+x,y,3/2-z; (xix) 1-x,-y,2-z; (xx) 1/2-x,-y,1/2+z; (xxi) 1/2-x,-y,-1/2+z

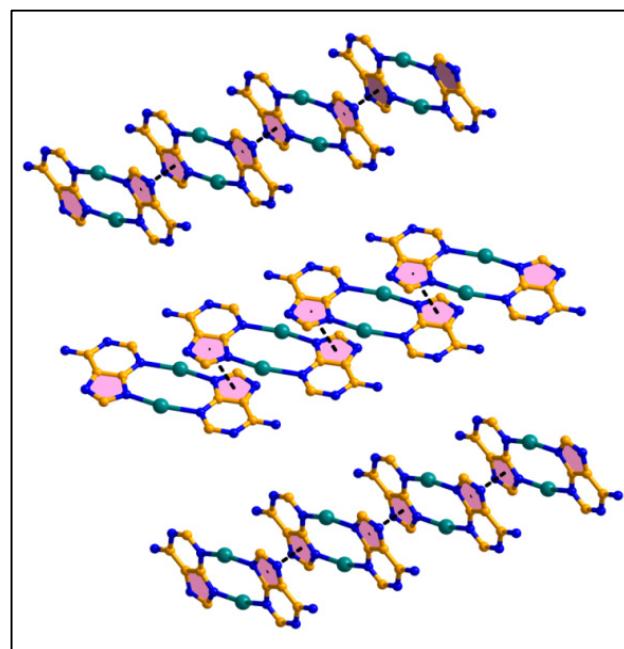


Figure S1: π - π stacking interaction between five membered rings of adenine moieties in complex 1.

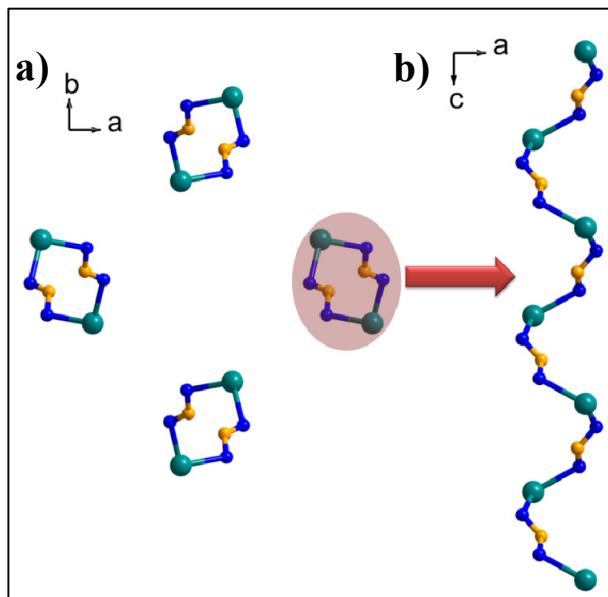


Figure S2: (a) Part of crystal lattice viewed along c axis. (b) Formation of helical architecture when highlighted region viewed along b axis.

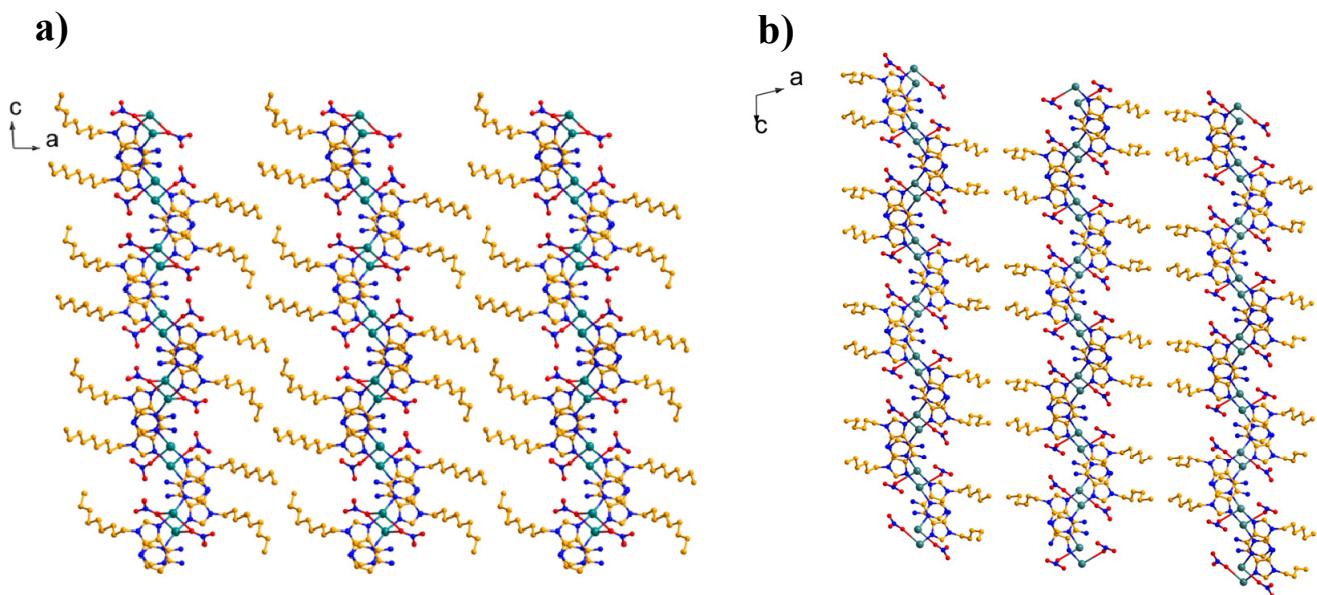


Figure S3: (a and b) 3D lattice of complex 3 and 4 respectively, showing the corresponding Nonyl /hexyl chain flanked from both side.

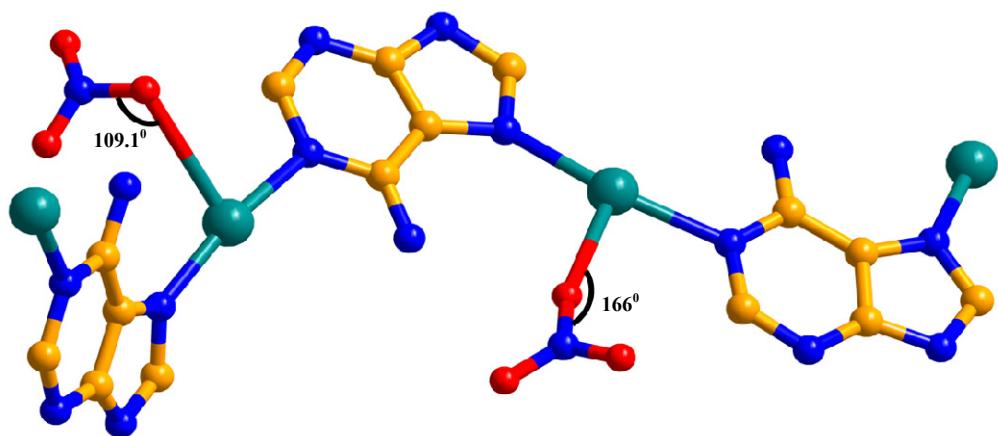


Figure S4: Deviation in Ag-O-N bond angle at adjacent silver ions coordinated with nitrate group in 4.

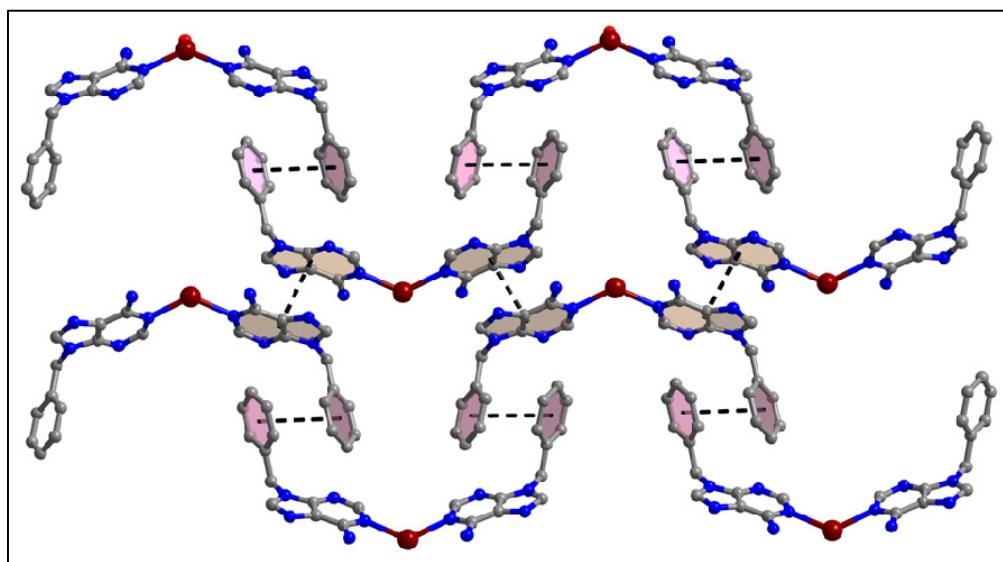


Figure S5: π - π stacking interaction between six membered rings of adenine moieties in **5**.

References:

1. C.S. Purohit, A. K. Mishra and S. Verma, *Inorg. Chem.* 2007, **46**, 8493
2. SAINT+, 6.02 ed.; Bruker AXS, Madison, WI, 1999.
3. G. M. Sheldrick., SADABS 2.0; University of Göttingen: Göttingen, Germany, 2000.
4. G. M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.